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14. ABSTRACT DNA is an abundant natural product with very good biodegradation properties and can be used to obtain gel polymer electrolytes (GPEs) with high ionic conductivity and good stability. This report presents results of developed GPE membranes based on DNA. The ionic conductivity results of the DNA-based membranes at room temperature were in the range of 10-3-10-5 S/cm and increased linearly as a function of temperature, obeying predominantly an Arrhenius relationship. The transmittance results in the UV-Vis region revealed transparency of 85-95%. Membranes of DNA with PEDOT, POEA and PB as well as DNA-CTMA and DNA-DODA were also obtained and characterized. High ionic conductivity results combined with transparency and adhesion to the electrodes showed that DNA-based GPEs are very promising materials to be used as solid electrolytes in electrochemical devices. To verify this applicability the membranes were used to obtain small electrochromic devices (ECDs), which were characterized by cyclic voltammetry, charge density and spectroscopic measurements. The obtained results showed a change of color from transparent to blue after potential application. Moreover the DNA was applied in small solar cells giving the conversion efficiency of 2.44%.					
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DNA-based electrochromic and photovoltaic cells

REPORT - FINAL

Award number: FA9550-09-1-0647

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Abstract

DNA is an abundant natural product with very good biodegradation properties and can be used to obtain gel polymer electrolytes (GPEs) with high ionic conductivity and good stability. This report presents results of developed GPE membranes based on DNA. The ionic conductivity results of the DNA-based membranes at room temperature were in the range of 10^{-3} - 10^{-5} S/cm and increased linearly as a function of temperature, obeying predominantly an Arrhenius relationship. The transmittance results in the UV-Vis region revealed transparency of 85-95%. Membranes of DNA with PEDOT, POEA and PB as well as DNA-CTMA and DNA-DODA were also obtained and characterized. High ionic conductivity results combined with transparency and adhesion to the electrodes showed that DNA-based GPEs are very promising materials to be used as solid electrolytes in electrochemical devices. To verify this applicability the membranes were used to obtain small electrochromic devices (ECDs), which were characterized by cyclic voltammetry, charge density and spectroscopic measurements. The obtained results showed a change of color from transparent to blue after potential application. Moreover the DNA was applied in small solar cells giving the conversion efficiency of 2.44%, higher when compared with the similar solar cells without DNA.

Key words: gel electrolyte, ionic conductivity, gelatin, DNA, electrochromic devices
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1. Introduction

The use of inexhaustible sources of alternative energies, such as solar and wind systems, requires the development of new materials for an efficient implementation. Within this demand, the study of solid ionic conductive materials has gained great importance. Some

research areas, such as new types of memory and computer architecture, biomedical devices and microsensors to control air pollution, batteries, photochromic and electrochromic windows have benefited from the development of these materials [1-4]. The main advantage of solid polymer electrolytes (SPEs) is their ability to form thin films of very high surface area with high values of power density of devices. Also, under electrochemical cycling, polymer electrolytes remain stable, contrarily to the crystalline or vitreous materials [2,5].

Among different polymeric electrolytes new materials based on polysaccharides [6-8] and proteins [9,10], have received considerable attention in recent years. The change in the physical and chemical properties of natural polymers and the improvement of their functional characteristics can be performed by means of chemical reactions, such as etherification, esterification, grafting and crosslinking reactions or physical processes, like plasticization. The derivatization reactions involve the exchange or introduction of functional groups into macromolecules, leading to changes in the gelatinization and retrogradation properties of these materials. As an example, the modified starch can be obtained by introducing hydroxypropyl groups resulting in inter- and intramolecular hydrogen bonding interruption and, consequently, an increase in the amorphous phase [11]. The preparation of different blends based on natural polymers, like polysaccharides, such as cellulose, chitosan, starch etc. and their derivatives and gelatin, i.e., protein [6,7,9], allows for their processing in the film form with good mechanical properties, as well as adhesion to glass and metal surfaces.

As mentioned above, natural polymer-based plastics can be obtained through plasticization [12,13] or grafting [14] processes. The polymer electrolytes obtained by plasticization process with low molecular weight substances increase the values of the ionic conductivity of the formed blends. Although the mechanism is not well known yet, there is an interaction of ions with mobile specific sites along the polymer chain. Also the fact that a plasticizer separates the polymer chain enhances the assumptions about their important role in the increase in the ionic conductivity values [15].

Glycerol and water have been widely used as plasticizers for starch, reacting as polymer chain crosslinking and separating agents. These interactions may be the Van der Waals forces and hydrogen bonds formed due to polymer-polymer and polymer-plasticizer interactions [12]. To obtain gelatin-based ionic conducting membranes, formaldehyde can be used to crosslink the chains, increasing the stability of the plasticizer and, consequently, improving the ionic conductivity of the samples.

The ability of proteins to form films or membranes has been known for many years [16]. Gelatin (Fig. 1) is one of the first materials to be used in the production of movies. This

protein is very promising in this area since it is an abundant and biodegradable material, has low cost and good film forming properties, is not toxic and forms transparent solutions with high viscosity [17]. An important factor to be considered is that these films are obtained by solubilization, heat and dehydration of collagen, which leads to a distortion of a partial triple helix of this macromolecule. To improve the functional properties of these films, crosslinking agents, as formaldehyde, glutaraldehyde or glyoxal are used [18,19].

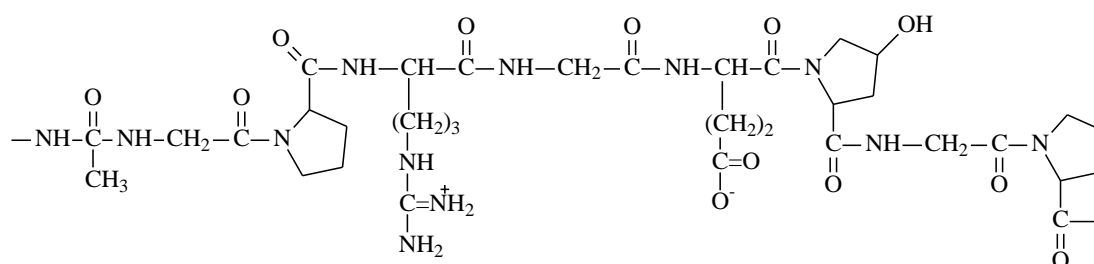


Figure 1. Representative structure of gelatin.

Last years it was possible to observe a growing interest in measuring the local electrical and structural properties of biological systems and biologically important molecules as DNA (Figure 2). Fink and Schonenberger [20] discovered that the transport of electric current by DNA is as efficient as that of a good semiconductor. Shimomura et al. [21] reported that the intercalation of some dyes in Langmuir-Blodgett films (LB) of DNA also leads to the obtaining materials with good photoconductive properties. Hagen et al. [22] presented results of the improvement in the electroluminescent properties of OLEDs (Organic Light Emitting Diodes) using modified DNA, which is soluble in organic solvents. OLEDs containing modified DNA were called BioLEDs. The results feed back into investigations into the optical properties of these materials and how the molecules can be engineered to create a new class of designed biomaterials. Apart from their potential relevance to biology, the study of these systems has revealed new physical phenomena, characteristic of the highly-fluctuating micro and nano world.

Charge migration in DNA is a subject of intense current studies partially motivated by various potential applications ranging from functional nanoscale electronic devices to long-range detection of DNA damage. A key structural element, which makes DNA an interesting medium for long-range charge transfer, is the array of stacked base pairs in the interior of the double helix with a stacking distance of ~ 3.4 Å [23]. The overlapping π -orbitals of the nucleobases provide a pathway for the motion of charge carriers generated on the stack. This “ π -pathway” resembles the columnar stacking of macrocyclic cores in mesomorphic discotic

materials such as triphenylenes or phthalocyanines, which are known to have similar stacking distances (3.5 ± 0.1 Å) as those found in DNA. An important factor governing charge transport in π -stacked systems is the electronic coupling between neighboring sites [24].

An important breakthrough in DNA science which has made practical applications possible was the obtaining of excellent optical quality thin films of DNA by N. Ogata [25-27] group in Japan and US Air Force researchers at Wright Patterson Labs [28]. However the assessment of these applications requires fundamental studies on DNA in solid state, in which the behavior is expected to be different than that in solution.

DNA is an acid, but during its extraction from salmon sperm and purification it is obtained in the form of sodium salt. This salt can then react with CTMA (hexadecyltrimethyl ammonium chloride or cetyltrimethylammonium chloride) leading to the formation of DNA-CTMA complex, as shown in Figure 2. In the complex of DNA-CTMA there occurs an exchange of Na^+ ion by the CTMA, providing new physical and optical properties to the DNA. This modification makes it soluble in organic solvents and leads to the formation of membranes, which present good transparency and flexibility.

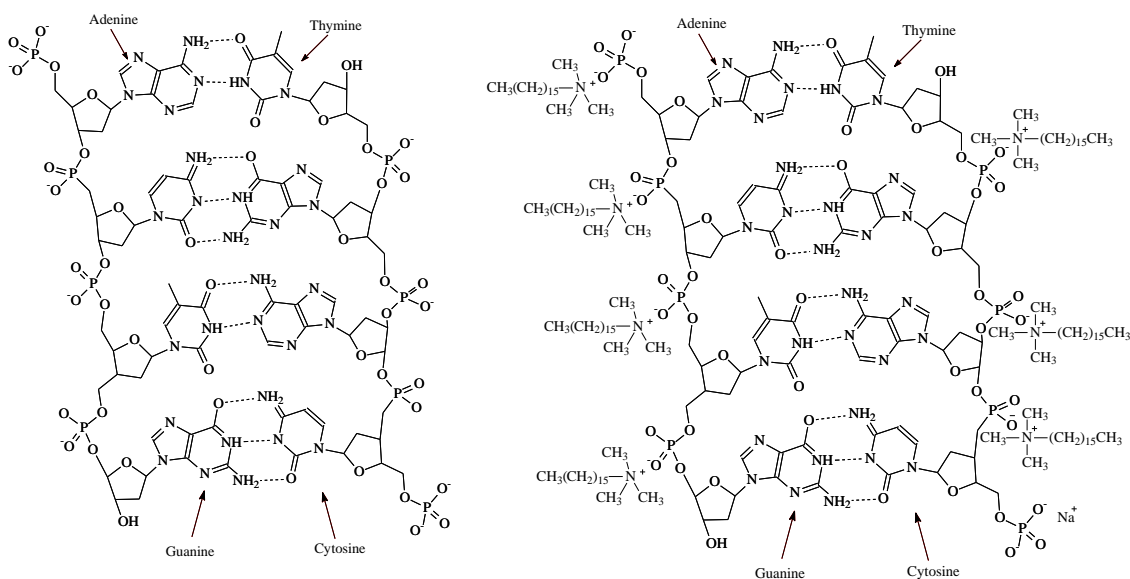


Figure 2. Representative structure of DNA (left) and DNA-CTMA (right).

Electrochromic materials have the property of changing color when either a voltage is applied across them or a current is passed through them. This color change should be reversible when the polarity of either the voltage or the current is reversed. Devices made with these materials can find their main application in the efficient use of energy by

controlling the flow of light and heat passing through the glazing of buildings, vehicles, trains, aircrafts etc. [1] and also as automotive rearview mirrors [2].

Modified DNA-based conducting electrolytes were developed and used to build and tested in small area ECDs with the glass/ITO/WO₃/DNA-based electrolyte/CeO₂-TiO₂/ITO/glass configuration [29].

2. Experimental

2.1 Gel polymeric electrolytes

The electrolytes were prepared according to the following method: 0.2-0.5g of salmon DNA (Ogata Research Laboratory, Japan) were dispersed in 15 mL of water and heated under magnetic stirring for a few minutes up to 50 °C for complete dissolution. Then, 0.015 – 0.35 g of salt (LiClO₄, LiBF₄), 0.25 - 3.5 g of glycerol as plasticizer and 0.03-0.25 g of formaldehyde were added to this solution under stirring. This viscous solution was cooled down to 30 °C and poured on Petri plates to form transparent membranes. Blend samples were also prepared by the addition of other macromolecules (gelatin), synthetic polymers, such as poly(ethylene dioxide thiophene) (PEDOT) nad poly(orthoetoxyaniline) (POEA), and inorganic dye (Prussian Blue).

Samples with different compositions were prepared and characterized. Their compositions are shown in Tables 1, 2 and 3.

Table 1. DNA-based samples compositions

DNA		LiClO ₄		Glycerol		HCHO		
0.2	41.7	0	0	0.25	52.1	0.03	6.3	1.1x10 ⁻⁵
0.2	40.4	0.015	3.0	0.25	50.5	0.03	6.1	3.5x10 ⁻⁵
0.5	28.6	0	0	1.25	71.4	0	0	3.4x10 ⁻⁴

Table 2. DNA-based samples compositions

Sample	DNA		Glycerol		LiClO ₄		σ S/cm	T °C
	g	wt %	g	wt %	g	wt %		
S1	0.2	13.8	1.25	86.2	0	0.0	3.9x10 ⁻⁶	21.5
S2	0.2	13.7	1.25	85.3	0.015	1.0	8.5x10 ⁻⁶	20.9
S3	0.5	28.6	1.25	71.4	0	0.0	3.0x10 ⁻⁵	24.1
S4	0.5	28.3	1.25	70.8	0.015	0.8	1.2x10 ⁻⁴	26.6
S5	0.5	28.2	1.25	70.6	0.02	1.1	1.5x10 ⁻⁴	23.5

Table 3. DNA-based samples compositions

Macromolecule		Salt		Plasticizer		Crosslinking agent		σ
g	wt. %	g	wt. %	g	wt. %	g	wt. %	S/cm (25°C)
DNA		LiClO₄		Glycerol		HCHO		
0.2	41.7	0	0	0.25	52.1	0.03	6.3	1.1×10^{-5}
0.2	40.4	0.015	3.0	0.25	50.5	0.03	6.1	3.5×10^{-5}
0.5	28.6	0	0	1.25	71.4	0	0	3.4×10^{-4}
DNA		Prussian Blue		Glycerol		HCHO		
0.5	66.0	0.0075	1.0	0.25	33.0	0	0	2.2×10^{-4}
DNA		PEDOT		Glycerol		HCHO		
0.5	65.4	0.015	2.0	0.25	32.6	0	0	1.2×10^{-3}
DNA		Red Gelatin		Glycerol		HCHO		
0.5	55.6	0.15	16.7	0.25	27.8	0	0	5.5×10^{-4}

Moreover samples of DNA-CTMA were also prepared by dissolving DNA in water and adding cetyl trimethyl ammonium bromide or cetyl trimethyl ammonium chloride (Aldrich) (CTMA). The solution was then stirred until the precipitation of a white solid, which was separated by decantation and filtered and washed with Milli-Q water until the removal of the surfactant. The white solid was then dried in the dessicator and submitted to analysis.

2.2 Electrochromic devices

Electrochromic devices with the glass/ITO/WO₃/DNA-based electrolyte/CeO₂-TiO₂/ITO/glass configuration were obtained by assembling the 2 pieces of coated glasses. DNA-based electrolytes in the form of membranes were deposited on glass/ITO/WO₃ coatings and 1 cm free space was left for the electrical contact. The other coated substrate was then pressed onto the membrane in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape was glued to the free edge of each substrate for electrical connection. The mounted cells were finally sealed with protective tape.

2.3 Characterization techniques

Impedance spectroscopy measurements were used to determine the electrolyte ionic conductivity and its frequency behavior. A round piece of the electrolyte (diameter of 2 cm and thickness of 0.01-0.5 mm) was pressed between two stainless steel electrodes. The system was installed in a glass cell under vacuum. The measurements were taken with an Autolab instrument equipped with either an FRA2 module or Solartron 1260, applying a voltage of 5 mV rms amplitude in the frequency range of 10^6 Hz to 10 mHz.

The UV-Vis optical spectra were recorded with an Agilent Spectrophotometer Instrument between 200 and 1100 nm.

The charge density measurements were performed with Autolab 302N with FRA 2 module applying -3.5/3.0V potentials for 30 s.

3. Results and discussion

During the development of this project the results obtained with the DNA membranes with different compositions as plasticized samples, with different salts, with different additives as either poly(ortho ethoxyaniline) (POEA), poly(ethylene dioxythiophene) (PEDOT) or Prussian Blue (PB) were analyzed and already published. The references of the papers are cited below.

- ✓ A. Pawlicka, A. Firmino, D. Vieira, J.G. Grote, F. Kajzar, SPIE, 7487 (2009) 74870J-74871 - 74870J-74810.
- ✓ Pawlicka, A. Firmino, J.G. Grote, Ion-conducting membranes based on gelatin and DNA, in: SPIE Newsroom, SPIE, 2009, pp. 1-2.
- ✓ Firmino, A.; Grote, J. G.; Kajzar, F.; M'Peko, J.-C.; Pawlicka, A., DNA-based ionic conducting membranes. *Journal of Applied Physics* **2011**, *110*, 033704.
- ✓ A. Firmino, J. G. Grote, F. Kajzar, I. Rau and A. Pawlicka, *Application of DNA in electrochromic cells with switchable transmission. Nonlinear Optics & Quantum Optics*; accepted.
- ✓ A.Pawlicka, F.Sentanin, A.Firmino, J.G. Grote, F. Kajzar, I. Rau. *Ionically conducting DNA-based membranes for electrochromic devices. Synthetic Metals*, **2011**, *161* (21-22), 2329– 2334.

Also the obtained results were presented in the oral form during the international conferences, as listed below.

1. SPIE-Europe Security and Defence; *Gelatin and DNA-based ionic conducting membranes*. 31/08-03/09/2009. Berlin, Germany.
2. Xth International Conference on Frontiers of Polymers and Advanced Materials (Xth ICFPAM); *Gelatin and DNA-based ionic conducting membranes*. 28/09-2/10/2009. Santiago, Chile.
3. 2010 International Biotronics Workshop; *DNA-based ionic conducting membranes for electrochromic devices*. 29/03-02/04/2010, San Juan, Puerto Rico. USA.
4. 3rd International Conference on Functional Materials and Devices (ICFMD). *DNA-based membranes with ionic conducting properties*. 14-17/06/2010. Kuala Terengganu, Malaysia.
5. International Symposium on Polymer Electrolytes (ISPE-12). *DNA-based membranes with ionic conducting properties*. 29/08-03/09/2010. Padova, Italy.
6. XIth International Conference on Frontiers of Polymers and Advanced Materials (ICFPAM). *Natural macromolecules based blends with ionic conductivity properties*. 22-27/05/2011, Pretoria, South Africa.
7. 18th International Conference on Solid State Ionics (SSI-18). *DNA-based membranes for electrochromic devices*. 03-08/07/2011, Warszawa, Poland.
8. International Workshop on Nano and Bio-Photonics (IWNBP) and French-Korean Meeting on Functional Material for Organic Optics, Electronics, and Devices (FUNMOOD). *Electrical measurements of solid state membranes containing DNA*. 23-28/10/2011, Saint Germain au Mont d'Or, France.

Description of some results

Results of blends of DNA with POEA, PEDOT and Prussian Blue membranes are showed below. Figure 3 show the pictures of the membranes of DNA and modified DNA with PEDOT, PB and POEA. As can be observed from this figure all the membranes are transparent and the membranes containing the additives have a blue coloration due to the additive. More intense blue is seen for the DNA-PB samples and gray color to the DNA-PEDOT samples.

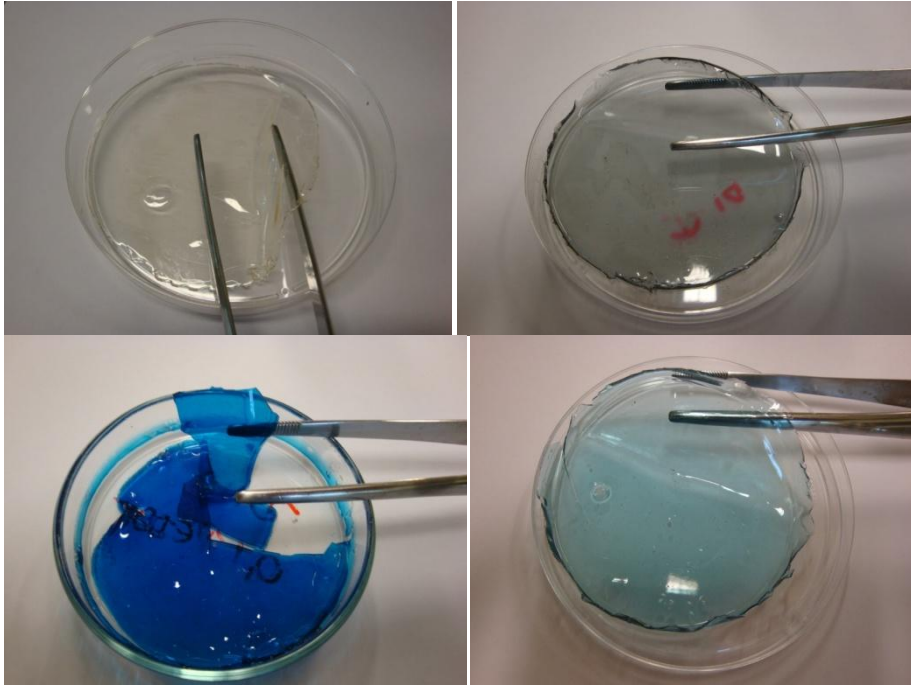


Figure 3. Pictures of DNA, DNA-PEDOT, DNA-Prussian Blue and DNA-POEA membranes.

The X-ray diffraction (Fig. 4) results reveal a semi-crystalline structure of the membranes and UV-Vis analysis a decrease of transmittance values after addition of conducting polymer molecules or PB (Fig. 5).

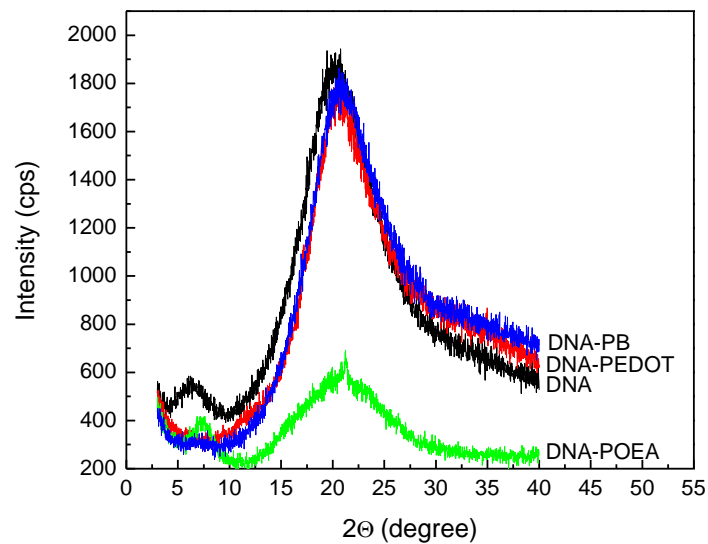


Figure 4. X-Ray diffractograms of DNA, DNA-Prussian Blue and DNA-PEDOT membranes on silicon wafer.

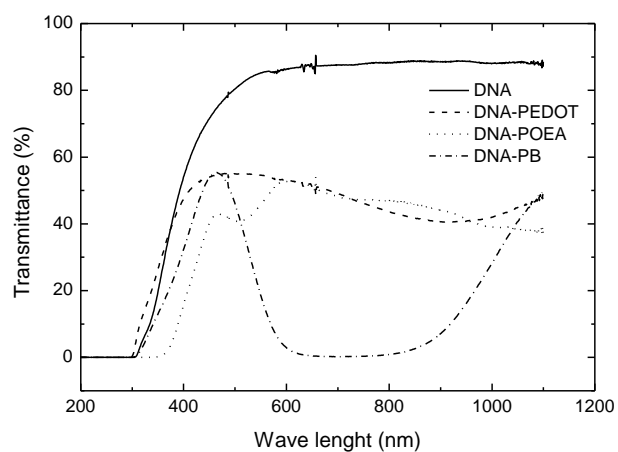


Figure 5. UV-Vis spectra of DNA, DNA-PEDOT, -POEA and -Prussian Blue membranes.

The thermal analyses are showed on Fig. 6 and 7. An increase of the thermal stability is observed after addition either of PEDOT, POEA or PB. The best thermal stability up to 100°C was confirmed for the samples of DNA-PEDOT.

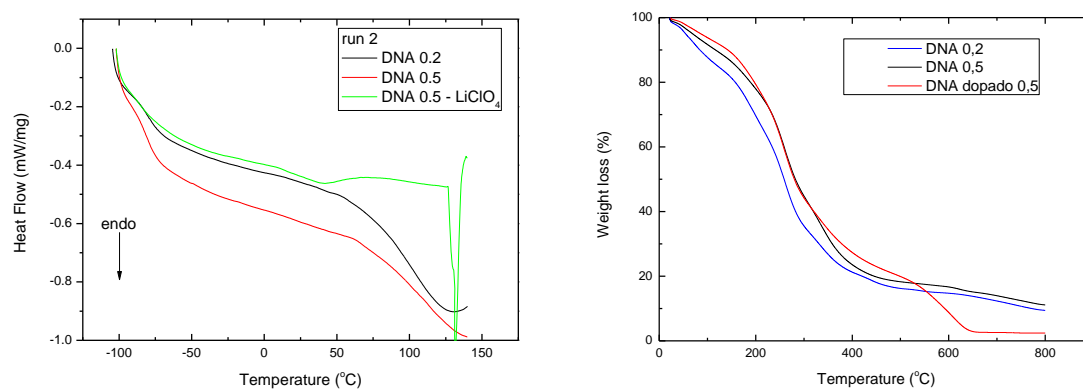


Figure 6. DSC (left) and TGA (right) of DNA and DNA-LiClO₄ samples.

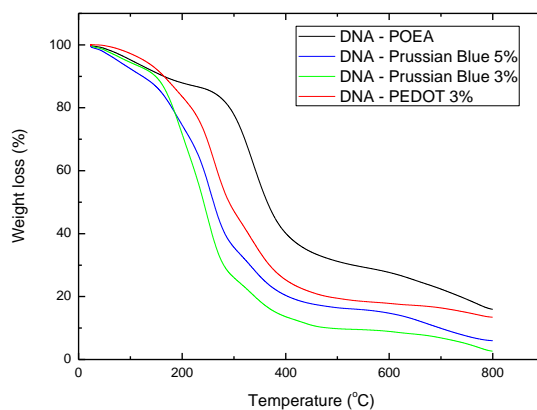


Figure 7. TGA of DNA, DNA-POEA, DNA-Prussian Blue, DNA-PEDOT samples.

The data of electrical measurements of the blends samples of DNA with PEDOT, POEA and Prussian Blue (below) were obtained by impedance measurement from room to 80°C. The results in Nyquist plots are showed on Figures 8 and 9 and the conductivity results as a function of temperature are showed in Fig. 10. From this figure one can observe an increase of the ionic conductivity as a function of temperature and also an increase as a function of additive. The best results of 10^{-3} S/cm were obtained for the samples of DNA-PEDOT.

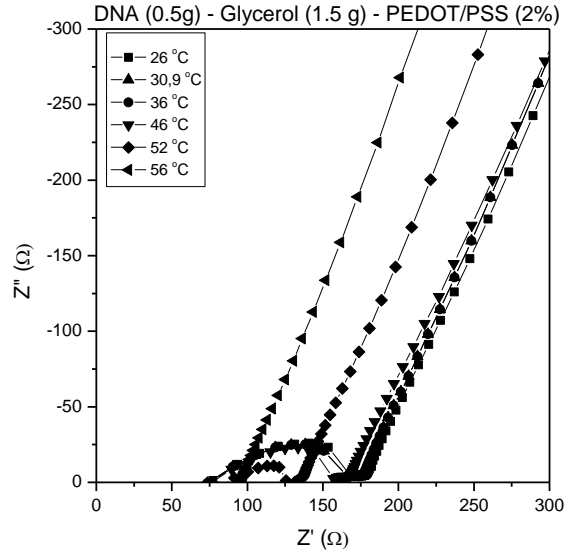


Figure 8 – Nyquist plot of DNA-PEDOT/PSS (left graph) and DNA-POEA (right graph) membranes at different temperatures.

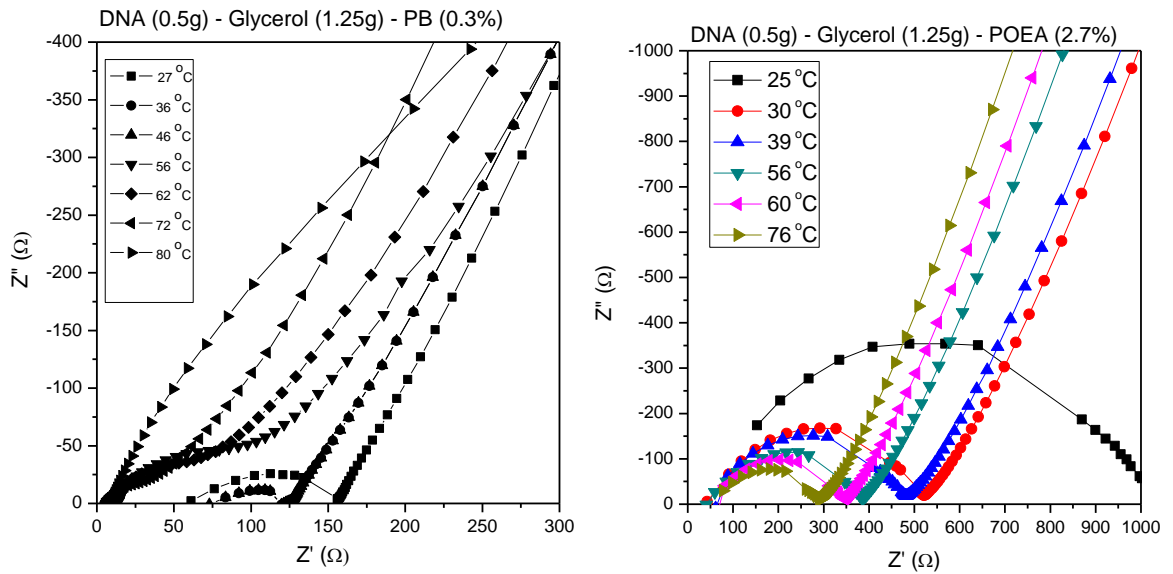


Figure 9 – Nyquist plot of DNA-PB membrane at different temperatures.

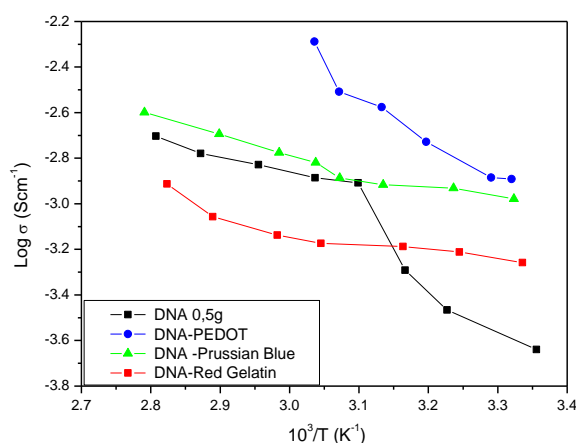


Figure 10. Ionic conductivity values of DNA- PEDOT, DNA-red gelatin and DNA-Prussian Blue.

Aiming to compare the thermal analysis with electrical measurements new impedance measurements as a function of temperature of the blends samples of DNA with poly(ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS), poly(orthoethoxy aniline) (POEA) and Prussian Blue (PB) were performed from 80 K to 360 K. From these data one can observe a start of charge carries movement at about 180 - 240 K, depending on the sample (Figure 11 and 12) which increases with temperature.

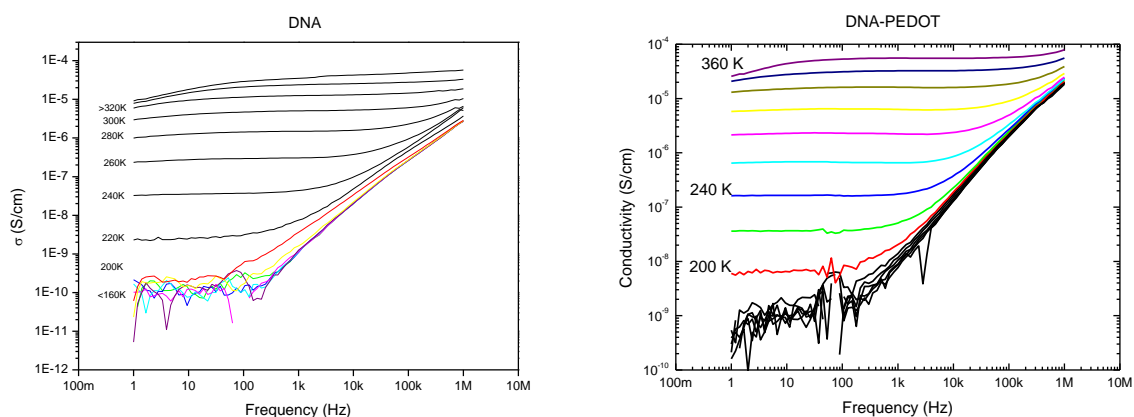


Figure 11 – Conductivity as a function of frequency plot of DNA (left graph) and DNA-PEDOT/PSS (right graph) membranes at different temperatures.

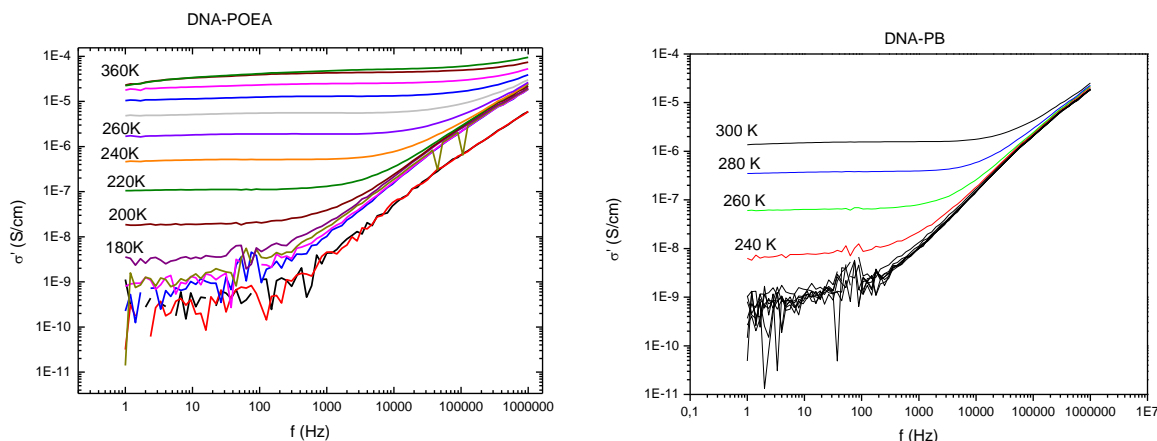


Figure 12 – Conductivity as a function of frequency plot of DNA-POEA (left graph) and DNA-PB (right graph) membranes at different temperatures.

The samples of DNA-PEDOT were also analysed by impedance measurements after green laser irradiation. The obtained results are showed below (Fig. 13). From these measurements it can be stated a decrease of the AC and DC conductivity and an increase of the Tg after green light irradiation due probably to the increase of the crystallinity of the samples.

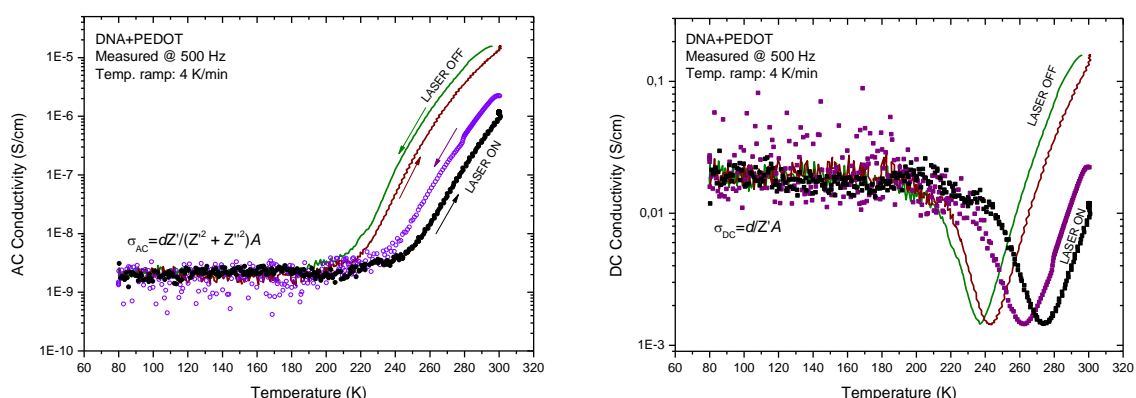


Figure 13 – AC (left graph) and DC (right graph) conductivity as a function of temperature of DNA-PEDOT/PSS membranes irradiated with green laser.

Also the DNA-PEDOT:PSS membrane sample was submitted to AC conductivity measurement as a function of time. The result is showed on Fig. 14. Also in this case an decrease of the conductivity as a function of time at 300 K is observed. This can be due to the rearrangement of the polymeric chains and/or loss of the residual water which help the charge carrier species displacement.

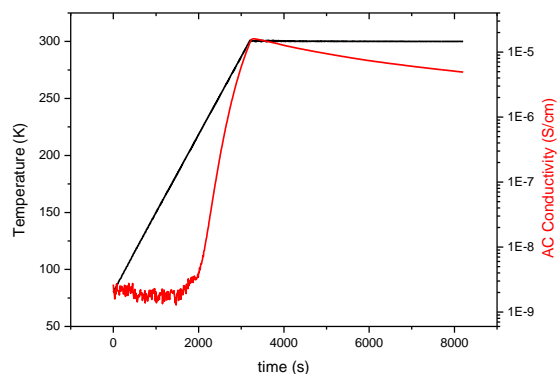


Figure 14 – Temperature evolution of AC conductivity as a function of time of DNA-PEDOT:PSS membranes.

Moreover some first resistance analysis of DNA-PB samples in two different measurements modes were performed (Fig. 15).

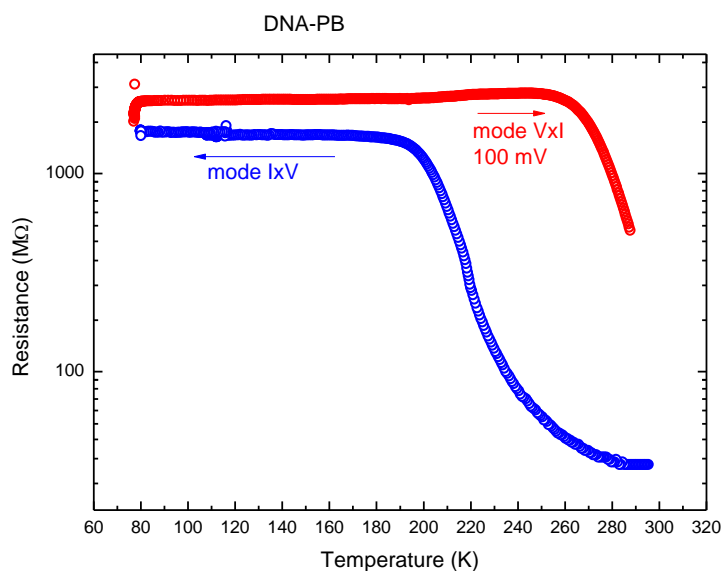


Figure 15 – Resistance as the function of temperature for the samples of DNA-PB for the I vs. V and V vs. I modes.

The membranes were also submitted to DMA thermal analysis (Fig. 16) from which was stated a glass transition temperature at 210 K and loss of elastic behavior at 320 K.

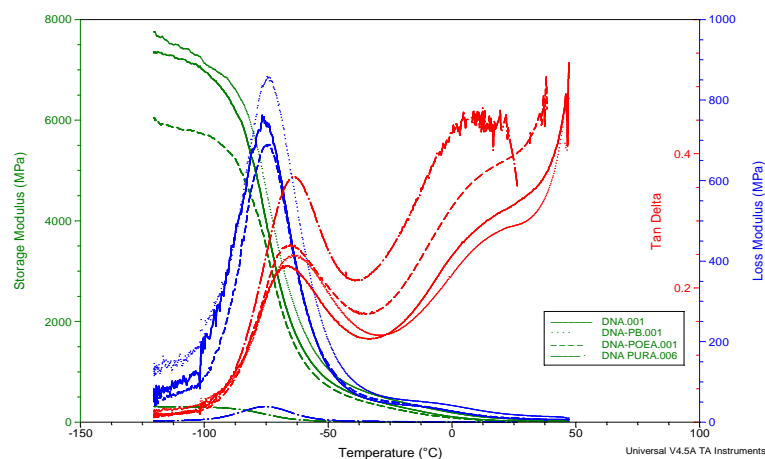


Figure 16 – DMA (storage modulus, loss modulus and $\tan \delta$) results as a function of temperature for the samples of DNA, DNA – PEDOT, -POEA and –PB.

The deformation of the membranes after submission to the DMA analysis can be also seen on pictures in Fig. 17 evidencing plastic behavior, i.e. permanence of deformation after submission to the mechanical force.

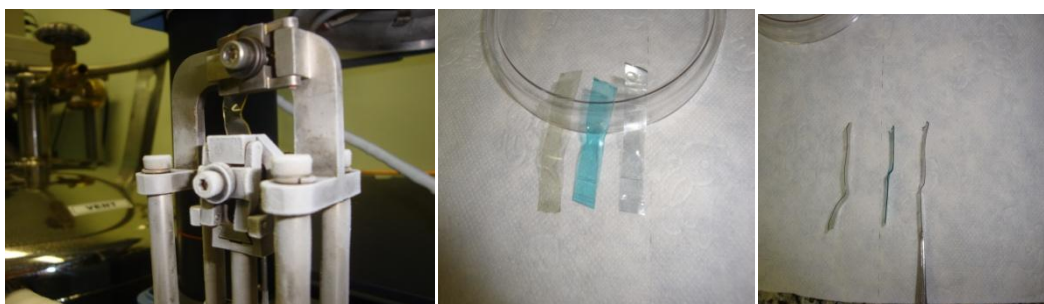


Figure 17 – Pictures of the sample in the DMA holder and after the analysis.

Results of electrochromic devices

The membranes samples were applied to the small electrochromic devices and characterized by electrochemical (Fig. 18) and spectroscopic measurements (Fig. 19). The voltammetry measurements present cathodic and anodic peaks, attributed to the insertion and extraction processes, respectively, i.e., coloration and bleaching of the devices. The charge density measurements reveal the insertion value of 3 mC/cm^2 and total reversibility of the system.

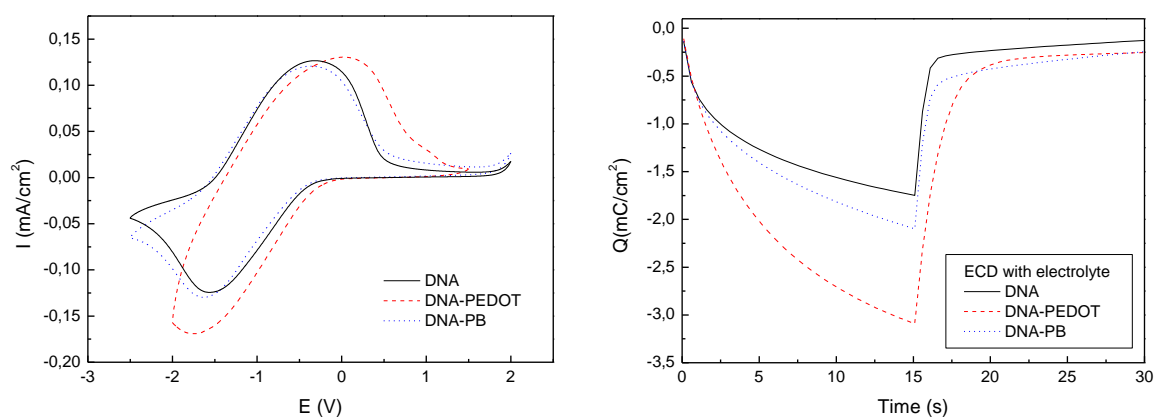


Figure 18. Cyclic voltammetry (left graph) and charge density(right graph) of ECD with glass/ITO/WO₃/DNA membrane/CeO₂-TiO₂/ITO/glass configuration.

The transmittance data showed in Fig. 19 reveal almost 20% of difference between color and bleaching states. The low transmittance for the bleached is due to the WO₃ and CeO₂-TiO₂ coatings.

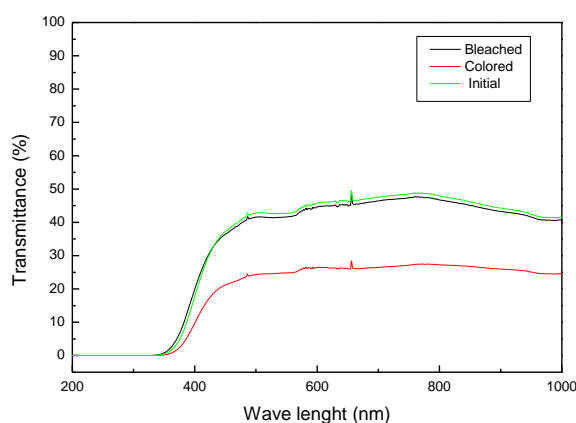


Figure 19. UV-Vis transmittance of ECD with glass/ITO/WO₃/DNA/CeO₂-TiO₂/ITO/glass configuration for bleached and colored states.

The pictures of the ECD with DNA electrolyte in transparent and colored states are showed in Fig. 20.

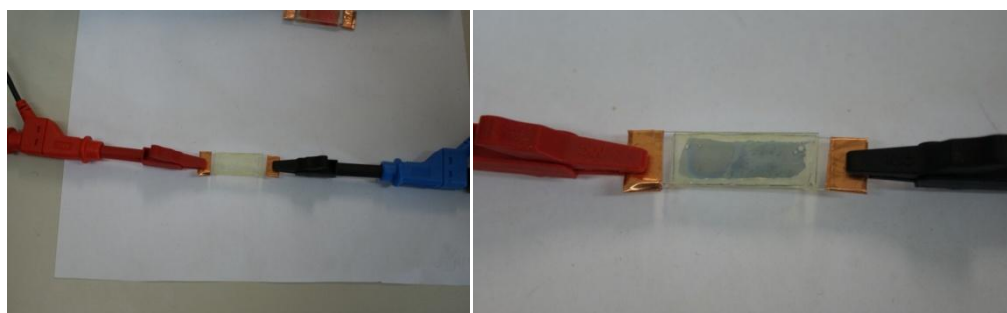


Figure 20. Pictures of bleached (left graph) and colored (right graph) ECD with glass/ITO/WO₃/DNA/CeO₂-TiO₂/ITO/glass configuration.

Results of DNA-CTMA synthesis and characterizations

Aiming to obtain DNA material with property of the solubility in organic solvents the DNA was submitted to the derivatization by substituting the Na^+ by cethyl trimethyl amine ion, resulting in the DNA-CTMA. The pictures of the obtained membranes are showed in Fig. 21.



Figure 21. Pictures of DNA-CTMA membranes with 6% of LiClO_4 , 6% of LiBF_4 and 1% of LiI (from left to right).

These samples were also characterized by FTIR measurements, as showed in Fig. 22. The evidence of the introduction of the CTMA ion are the bands at 2926 and 2846 cm^{-1} .

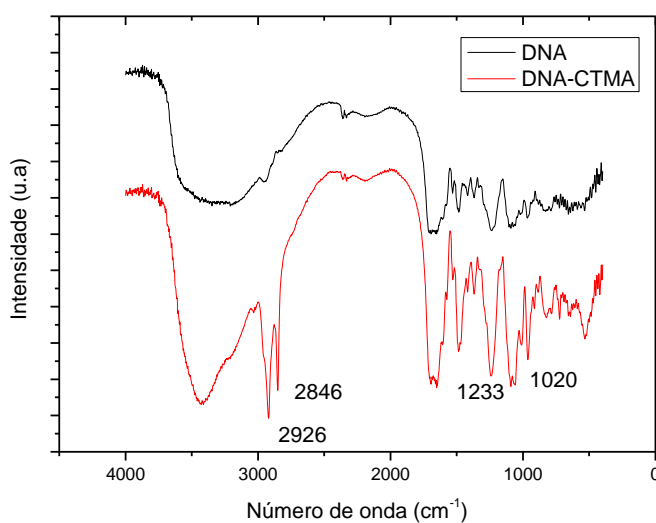


Figure 22. FTIR spectra of DNA and DNA-CTMA powder.

The DNA-CTMA membranes were also analyzed by UV-Vis measurements as showed on Fig. 23.

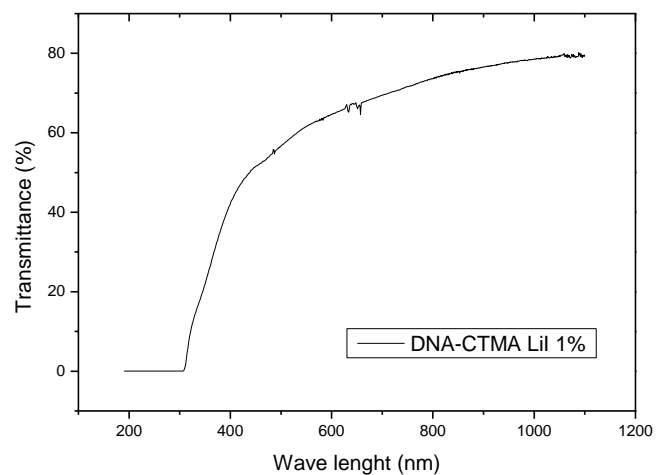


Figure 23. UV-Vis spectra of DNA-CTMA with 1% of LiI membrane.

These membranes presented also very uniform surface during the SEM analysis (Figures 24 and 25).

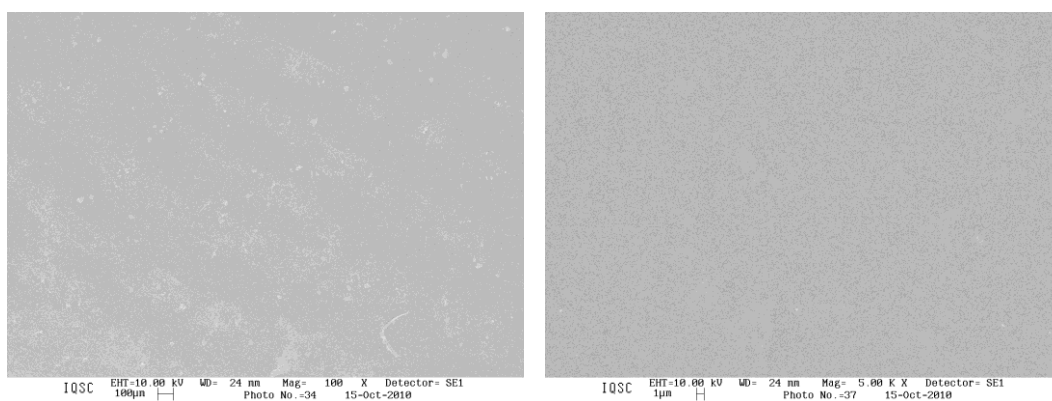


Figure 24. SEM pictures of DNA-CTMA membranes, 100x and 5,000x (from left to right).

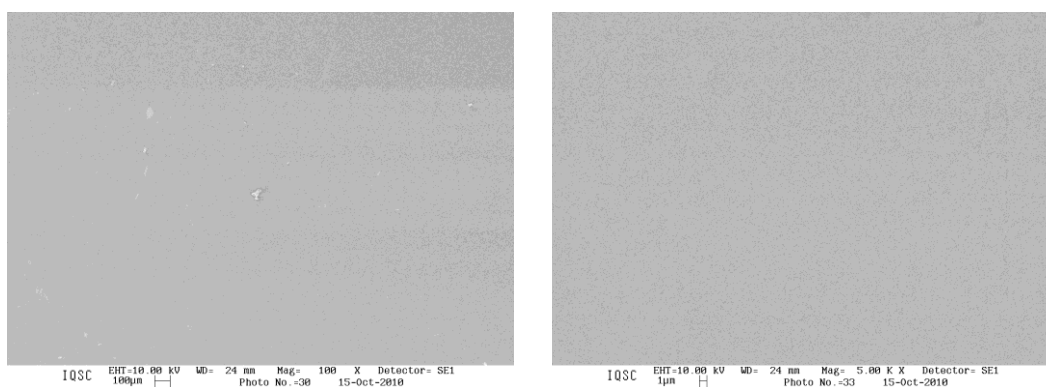


Figure 25. SEM pictures of DNA-CTMA with 1% of LiI membranes, 100x (left) and 5,000x (right).

Moreover, membranes of DNA-CTMA with salts LiClO_4 , LiI/I_2 and mixture of $\text{LiClO}_4/\text{LiI}$ were also obtained (Fig. 26).

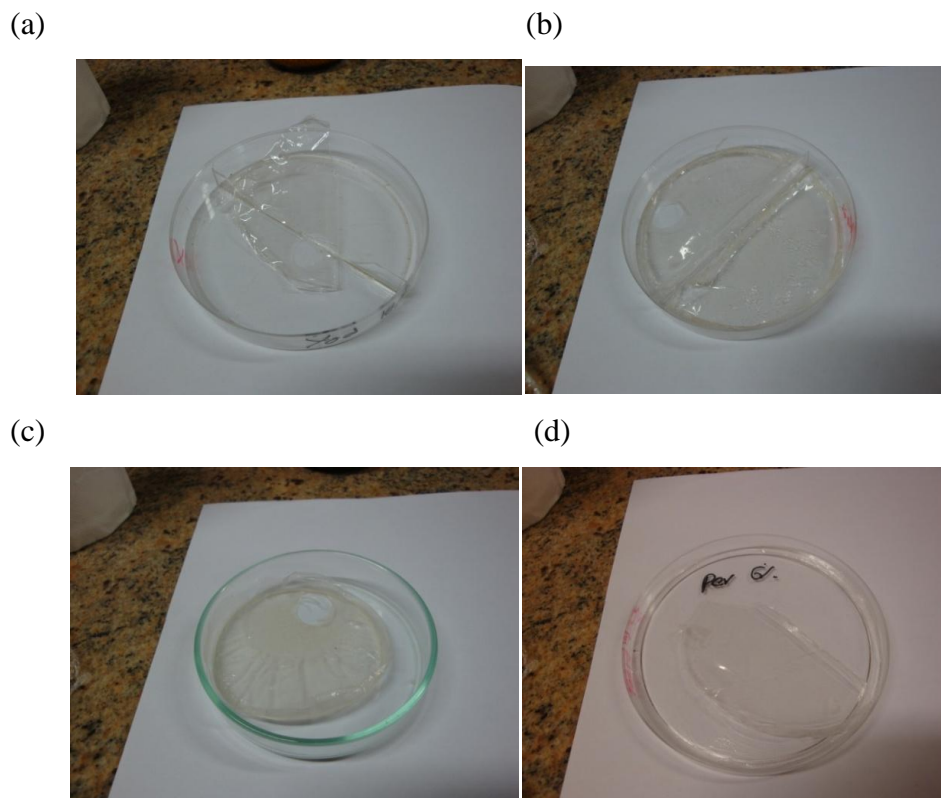


Figure 26 – DNA-CTMA samples with LiClO_4 at 7% (a), 9% (b), 10% (c) and LiI at 10% (d).

These membranes were characterized by impedance measurements, which revealed that the samples are thermally stable up to almost 100°C and the best results of ionic conductivity of $5 \times 10^{-3} \text{ S/cm}$ at room temperature were obtained with the samples of DNA-CTMA and containing LiClO_4 (Fig. 27) and LiI (Fig. 28).

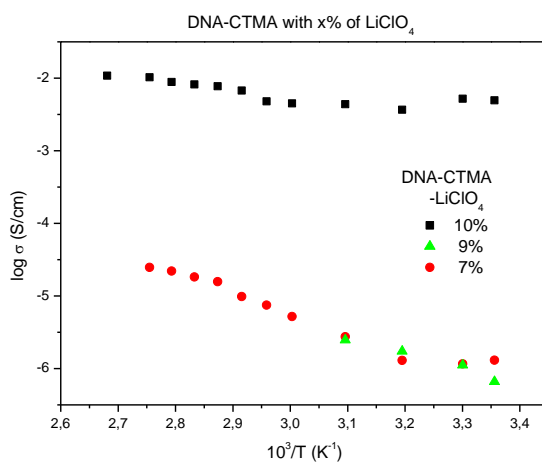


Figure 27 – Ionic conductivity measurements as a function of temperature of DNA-CTMA membranes with LiClO_4 at 7% (●), 9% (▲), 10% (■).

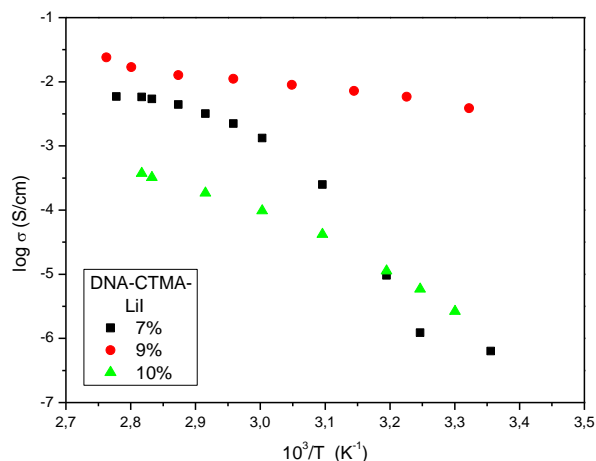


Figure 28 – Ionic conductivity measurements as a function of temperature of DNA-CTMA membranes with LiI at 7% (■), 9% (●) and 10% (▲).

The samples of DNA-CTMA and containing a mixture of LiClO₄-LiI, revealed conductivity values of 7×10^{-8} S/cm, considered lower when compared with samples containing only one salt (Fig. 29).

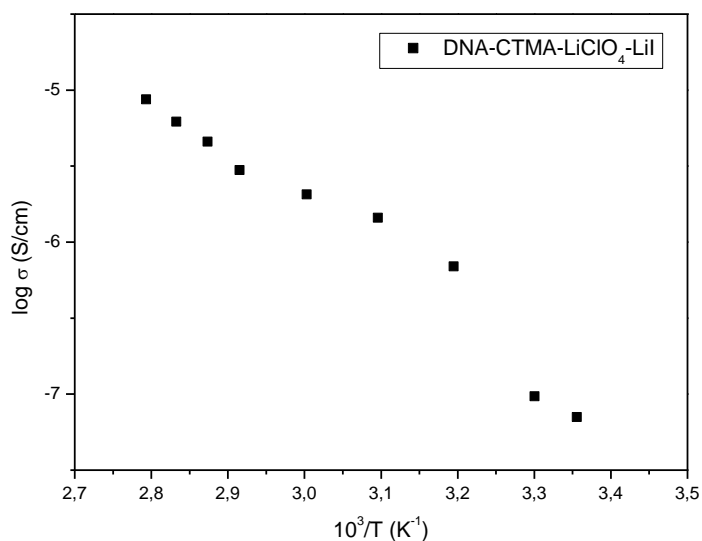


Figure 29 – Ionic conductivity measurements as a function of temperature of DNA-CTMA membranes with LiClO₄-LiI.

The membranes of DNA-CTMA-PEDOT, DNA-CTMA-POEA and DNA-CTMA-PB were also obtained and characterized by impedance measurements as showed in Fig. 30. The ionic conductivity of these samples was of 10^{-5} S/cm.

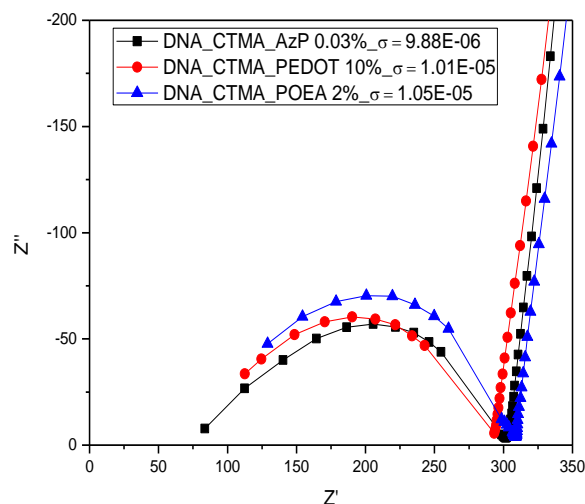


Figure 30 – Nyquist plot of DNA-CTMA_PEDOT, -POEA and -PB (AzP) membranes.

Results of DNA-CTMA synthesis and characterization are still performed. However small ECDs were assembled and submitted to electrochemical measurements as showed below (Fig. 31).

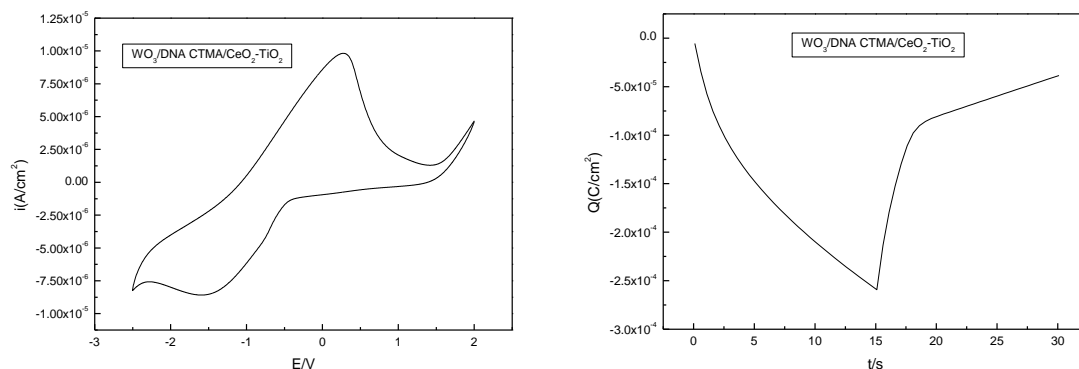


Figure 31. Cyclic voltammetry (left graph) and charge (right graph) of ECD with glass/ITO/ WO_3 /DNA-CTMA/ CeO_2 - TiO_2 /ITO/glass configuration.

Moreover electrochromic windows with WO_3 /DNA-CTMA-PEDOT and PB/ CeO_2 - TiO_2 were assembled and characterized by charge density, voltammetry and transmittance measurements. The preliminary results showed in Figures 32 and 33 revealed that the DNA-CTMA based membranes are promising as ionic conducting materials.

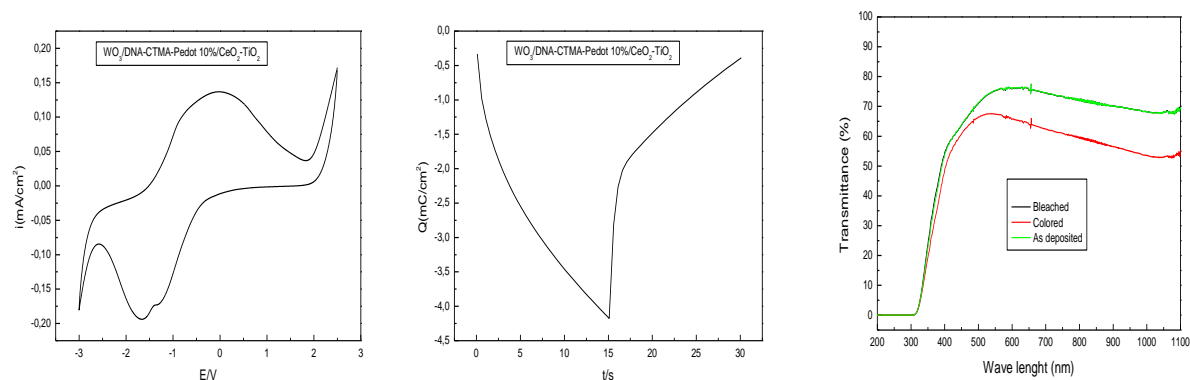


Figure 32. Cyclic voltammetry (left graph), charge (middle graph) and transmittance (right graph) results of ECD with $\text{WO}_3/\text{DNA-CTMA-PEDOT}/\text{CeO}_2\text{-TiO}_2$ configuration.

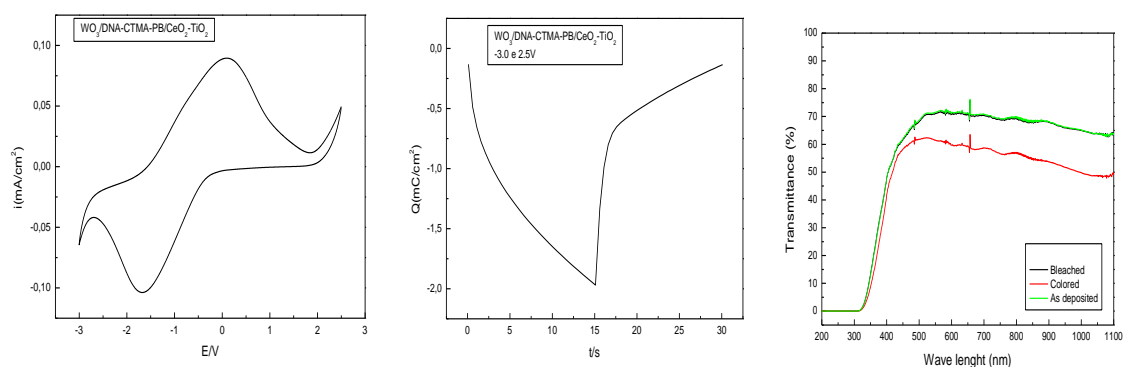


Figure 33. Cyclic voltammetry (left graph), charge (middle graph) and transmittance (right graph) results of ECD with $\text{WO}_3/\text{DNA-CTMA-PB}/\text{CeO}_2\text{-TiO}_2$ configuration.

Solar cells with DNA-CTMA

Aiming to obtain solar cells, DNA-CTMA was dissolved and applied in small devices but probably due to the lack of redox couple formation the obtained result was not satisfactory (Fig. 34). New approaches consisted of using DNA as hole and/or electron conductor were performed in the Prof. Dr. Ana Flavia Nogueira (UNICAMP) labs and now this investigation is continued.

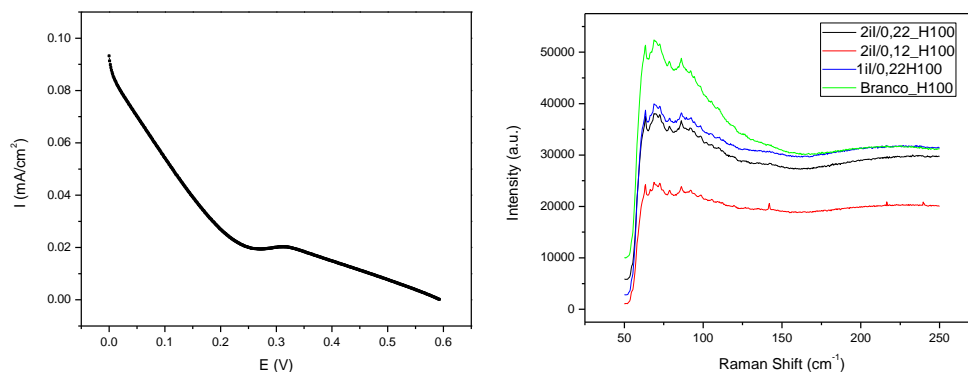


Figure 34 - Illumination curve at 100 mWcm^{-2} of solar cell based on TiO_2 /ruthenium dye and containing DNA-CTMA-based electrolyte (left graph) and Raman spectra of DNA-CTMA-based electrolyte (right graph).

Samples of DNA-DODA and containing LiClO_4 .

Aiming to turn the DNA soluble in acetone solution the macromolecule was modified with dioctadecyl dimethyl ammonium ion (DODA) showed on Fig. 35.

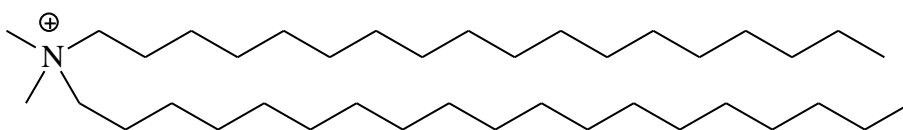


Figure 35 – Structure of DODA.

The conductivity results of the DNA-DODA and DNA-DODA with LiClO_4 membranes are showed on Fig. 36. From this figure one can observe a small increase of the conductivity values after salt addition.

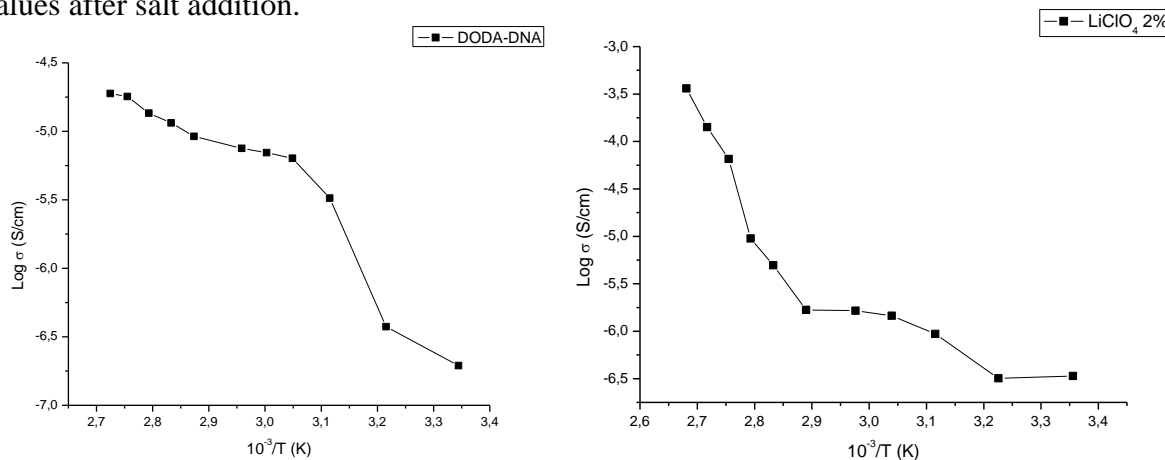


Figure 36 – Log of σ as a function of temperature for the DNA-DODA membranes.

Solar cells with DNA developed in Prof. Dr. Ana Flavia Nogueira (UNICAMP-Brazil) laboratory [the data are extracted from the reference 30].

The small solar cells were assembled with 0.20cm^2 of active area. A TiO_2 nanoporous film was prepared by doctor blading a small aliquot of a commercial colloidal suspension (Ti-Nanoxide T, Solaronix) onto a transparent conducting substrate (TCO; Hartford Glass Co., 8–12 Ω). The film were heated to 450°C for 30 min, originating a layer of $\sim 4\text{ }\mu\text{m}$ thickness as measured with a Tecnor Alpha-step 200 profilometer. Next the electrodes were immersed in a $1.5 \times 10^{-4}\text{ mol L}^{-1}$ solution of the sensitizer *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl- 4,4'-dicarboxylate)-ruthenium(II) (Ruthenium 535, Solaronix) in ethanol for 20 h at room temperature. Afterwards, the electrodes were washed with ethanol and dried in air. The DNA (denaturated; from water solution (DNA_agua) and from ethanol (DNA_EtOH) solution) was deposited over this film. The electrolyte film was deposited by casting a solution onto the dye-sensitized TiO_2 – DNA film and placing the substrate onto a hot plate at 40°C to remove residual water. Pt counter electrodes were pressed on the top of the polymer/electrolyte film. For comparison samples without DNA were also assembled and called “Branco”.

The I-V curves for the solar cells with and without DNA are showed in Fig. 37. This figure reveal the current density for the Branco, of 5.59 mA.cm^{-2} while for the cell containing denaturated DNA of 6.52 mA.cm^{-2} . Furthermore it is observed an increase in the current density after DNA addition, which can be due to the strong electrostatic interaction with TiO_2 , [31] and consequently desagration of the dye molecules. At this point it should be stated that DNA can contribute to the charge transport by hole or electrons movements. [32,33] From these measurements it was also stated a small increase of the open circuit potential, which can be due to the interaction of DNA nitrogen bases with TiO_2 .

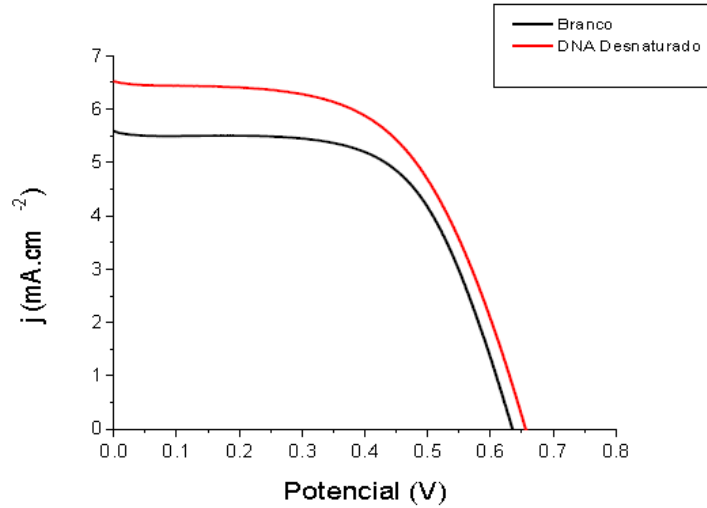


Figure 37. I-V curves of small solar cells under illumination intensity of 100 mW.cm^{-2} , with effective area of 0.25 cm^2 . Filter AM 1.5 and scan rate of 10 mV.s^{-1} . [30]

The principal parameters for these small solar cells are showed in the Table 4.

Table 4: Solar cell parameters (maximum power (P_{max}), current density of open circuit (I_{sc}), open circuit potential (V_{oc}), fullfilling factor (FF) and conversion efficiency (η)), under light intensity of 100 mW.cm^{-2} [30]

DSSCs	$P_{\text{max}} (\text{mW cm}^{-2})$	$I_{\text{sc}} (\text{mA cm}^{-2})$	$V_{\text{oc}} (\text{V})$	FF	$\eta (\%)$
Branco	2,19	5,59	0,64	0,62	2,19
DNA desnaturado	2,44	6,52	0,66	0,57	2,44

Again the device assembled without DNA showed a photocurrent of 3.35 mA.cm^{-2} . With the addition of DNA solution in ethanol, there was an increase in the photocurrent to 4.22 for the samples with DNA _agua and 3.81 for the sample DNA_EtOH. In this case it is observed a decrease of open circuit potential when compared to the Branco. The solar cells parameters for these samples are listed in Table 5 and the pictures of these solar cells are showed in Fig. 36..

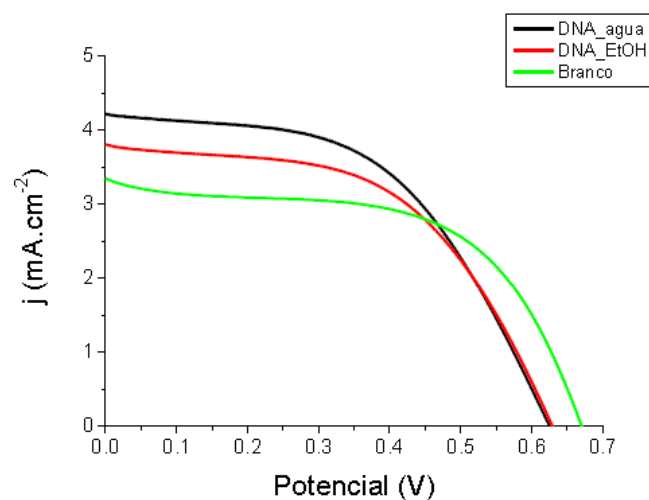


Figure 38. Curvas I-V das células sob intensidade de 100 mW.cm^{-2} , com área ativa de $0,25 \text{ cm}^2$. Foi utilizado filtro AM 1.5 e velocidade de varredura de 10 mV.s^{-1} . [30]

Table 5: Solar cell parameters (maximum power (P_{max}), current density of open circuit (I_{sc}), open circuit potential (V_{oc}), fullfiling factor (FF) and efficiency (η)), under light intensity of 100 mW.cm^{-2} [30]

DSSCs	$P_{\text{max}} (\text{mW cm}^{-2})$	$I_{\text{sc}} (\text{mA cm}^{-2})$	$V_{\text{oc}} (\text{V})$	FF	$\eta (\%)$
Branco	1,28	3,35	0,67	0,57	1,28
DNA em água	1,37	4,22	0,62	0,52	1,37
DNA em etanol	1,28	3,81	0,63	0,53	1,28



Figure 39: Picture of several solar cells with gold and silver electrodes. [30]

4. Conclusions

Polymer electrolytes based on DNA were prepared and analyzed by ionic conductivity, thermal and spectroscopic measurements. They were also tested in electrochromic devices and solar cells. The membranes based on DNA showed the best results of ionic conductivity of 3.4×10^{-4} S/cm for the samples without salt and containing 70% of glycerol. All analyzed samples were very transparent showing transmittance values in the Vis range of 85-95% depending on the sample. The use of these membranes in the electrochromic devices revealed that the gel electrolytes based on DNA showed higher inserted/extracted charge densities, when compared with the ECDs with gelatin-electrolytes. The ECD with red gelatin changed the color from red to deep red and the ECD with DNA-based electrolytes changed from transparent to blue. All the samples showed good adhesion to the glass and steel and are very promising materials to be used as solid electrolytes in electrochromic devices.

The first approach to apply these electrolytes to solar cells was unsuccessful due to the de-estrification reaction TiO_2 -dye, however the new approach developed by Prof. Dr. Ana Flavia Nogueira from DQ-UNICAMP revealed increase of the solar efficiency after DNA application over the TiO_2 thin film sensitized by *cis*-bis (isothiocyanate)-bis-(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium (II) dye. Moreover the samples of DNA-CTMA and DNA-DODA were prepared and characterized by impedance, FTIR, SEM and UV-Vis measurements. Also the samples of DNA-PEDOT, DNA-Prussian Blue and DNA-POEA were prepared and characterized by SEM, electrical measurements, thermal analysis and UV-Vis spectroscopy.

The project continues to be developed and one PhD, one master and one graduation student are working on this subject. New approaches by addition of other dye to the DNA membranes compositions are also planned. Moreover the DMA and electrical analysis are continued and soon will be submitted to the publications.

Acknowledgments

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